

Accuracy and Precision of PM_{2.5} and Co-pollutant Samplers Used in the Steubenville Comprehensive Air Monitoring Program

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SCAMP

- The goal of SCAMP is to examine the relationship between ambient PM_{2.5} concentrations and individual exposure and their relationship to health effects.
- To determine that the personal samplers and the Federal Reference Method samplers are equivalent, two personal samplers and one FRM sampler were collocated in the summer and fall of 2000.

SCAMP Funding

- US DOE NETL,
- Ohio Coal Development Office,
- EPRI,
- American Petroleum Institute,
- American Iron and Steel Institute,
- National Mining Association,
- Edison Electric Institute,
- National Institute of Environmental Health Services,
- USEPA, and
- CONSOL Energy Inc.

Measurement Error Model

$$Y_{ik} = \alpha_i + \beta_i \mu_k + \epsilon_{ik}$$

where

- Y_{ik} is the measurement made by the i^{th} of N samplers on the k^{th} of n parcels of air
- α_i and β_i describe the relative accuracy of the i^{th} sampler,
- μ_k is the true concentration of the k^{th} air parcel, and
- ϵ_{ik} is the random error from a Normal distribution with variance σ^2 .

The errors are assumed to be statistically independent between samplers and between measurements. These assumptions can be examined.

The μ_k can be treated as fixed or random quantities (depending on the type of analysis). If the μ_k are treated as random, the process variance is σ_μ^2 .

Measurement Error Models

- Two models:
 - Nonconstant bias model - Most general
 - Constant bias model - $\beta_1 = \beta_2 = \dots = \beta_N = 1$
 - MUST BE CHECKED!
- There are two ways to estimate these models:
 - Original data values - Process variance σ_μ^2 can be estimated.
 - Paired data values - Cannot estimate the process variance σ_μ^2 .

Study Design

The data will typically be in the form of an $n \times N$ matrix (items by methods):

$$\begin{matrix} y_{11} & y_{12} & \cdots & y_{1N} \\ y_{21} & y_{22} & \cdots & y_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ y_{n1} & y_{n2} & & y_{nN} \end{matrix}$$

merror R Package

- The *merror* R package is available at <http://www.r-project.org/> under contributed packages.
- *merror* implements the methods described in J. L. Jaech's *Statistical Analysis of Measurement Errors* (1985, Wiley, New York).
- *merror* has functions for computing estimates of the accuracy parameters α and β and for computing the maximum likelihood estimates for the precision using both the original data values and the paired data values.

merror R Package

The three functions you would typically use most often:

ncb.od Computes accuracy and precision estimates using the original data and does not assume a constant bias.

cb.pd Computes accuracy and precision estimates using the paired data which forces the assumption of a constant bias.

lrt Performs a likelihood ratio test for the β 's: $H_0 : \beta_1 = \beta_2 = \cdots = \beta_N = 1$.

In addition, there are three helper functions for accessing the errors under various models:

errors.ncb Errors for the nonconstant bias model

errors.cb Errors for the constant bias model ($\beta_1 = \beta_2 = \cdots = \beta_N = 1$)

errors.nb Errors for the no-bias model ($\alpha_1 = \alpha_2 = \cdots = \alpha_N = 0$ and $\beta_1 = \beta_2 = \cdots = \beta_N = 1$)

PM_{2.5} Data

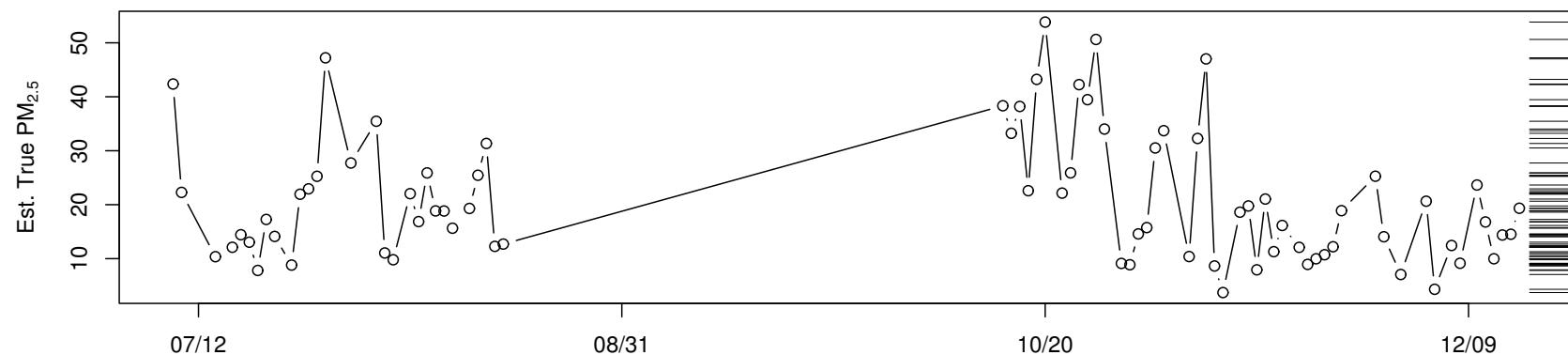
Seventy-seven complete sets (5 filters) of PM_{2.5} concentrations ($\mu\text{g m}^{-3}$) were collected. These data are included in the *merror* package.

| | ms.conc.1 | ws.conc.1 | ms.conc.2 | ws.conc.2 | frm |
|----|-----------|-----------|-----------|-----------|-------|
| 1 | 43.16 | 42.79 | 43.64 | 40.97 | 41.25 |
| 2 | 22.99 | 18.74 | 23.71 | 21.72 | 24.24 |
| 3 | 10.23 | 10.16 | 9.95 | 10.83 | 10.64 |
| 4 | 12.53 | 11.88 | 11.83 | 11.87 | 12.43 |
| 5 | 14.15 | 13.65 | 14.14 | 14.86 | 15.36 |
| 6 | 13.19 | 12.26 | 12.34 | 12.86 | 14.61 |
| 7 | 8.96 | 8.23 | 6.74 | 5.62 | 9.52 |
| 8 | 18.26 | 16.36 | 16.27 | 16.11 | 19.34 |
| 9 | 14.19 | 12.84 | 14.37 | 13.76 | 15.44 |
| 10 | 7.86 | 8.10 | 9.30 | 9.26 | 9.51 |
| 11 | 21.37 | 21.40 | 20.91 | 21.00 | 25.00 |
| 12 | 22.98 | 22.71 | 22.48 | 21.12 | 25.40 |
| 13 | 25.44 | 23.56 | 24.49 | 24.14 | 28.68 |
| 14 | 45.99 | 47.15 | 44.88 | 46.68 | 51.39 |
| 15 | 27.05 | 27.70 | 26.16 | 26.50 | 31.21 |
| 16 | 35.03 | 33.55 | 32.96 | 34.23 | 41.55 |
| 17 | 9.60 | 12.06 | 9.37 | 11.86 | 12.37 |
| 18 | 8.91 | 9.76 | 8.35 | 9.66 | 12.28 |
| 19 | 20.33 | 22.86 | 20.57 | 21.90 | 24.55 |
| 20 | 13.26 | 13.73 | 15.70 | 17.38 | 24.26 |
| 21 | 26.63 | 23.62 | 25.62 | 25.05 | 28.51 |
| 22 | 19.69 | 16.12 | 19.23 | 18.19 | 20.99 |
| 23 | 17.54 | 17.92 | 19.15 | 18.22 | 21.31 |
| 24 | 14.37 | 15.86 | 15.08 | 15.99 | 16.88 |
| 25 | 18.64 | 19.48 | 19.17 | 16.69 | 22.52 |
| 26 | 23.33 | 25.00 | 24.70 | 25.43 | 28.80 |
| 27 | 28.72 | 30.12 | 30.23 | 33.20 | 34.46 |
| 28 | 12.64 | 14.19 | 10.07 | 10.76 | 13.70 |

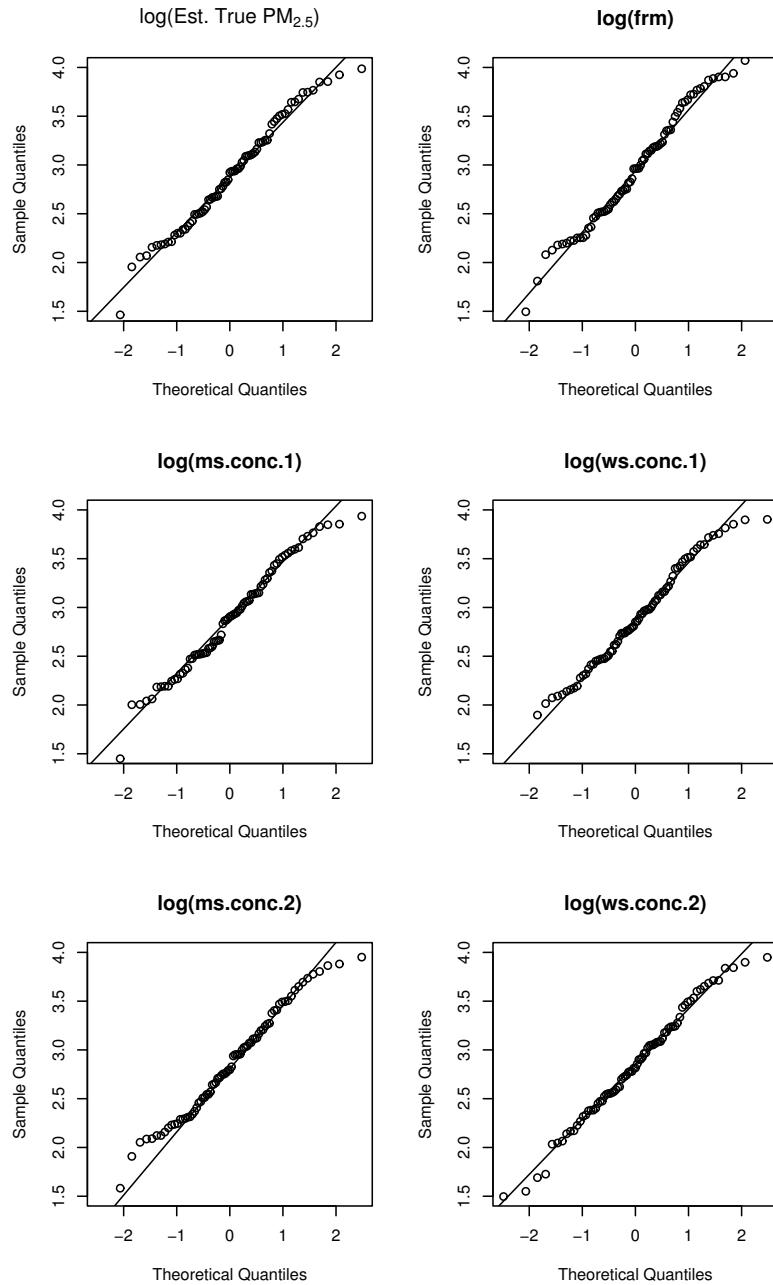
| | ms.conc.1 | ws.conc.1 | ms.conc.2 | ws.conc.2 | frm |
|----|-----------|-----------|-----------|-----------|-------|
| 29 | 12.46 | 11.81 | 12.75 | 10.83 | 15.66 |
| 30 | 36.46 | 36.79 | 37.04 | 37.34 | 44.03 |
| 31 | 30.96 | 32.08 | 32.14 | 31.78 | 39.21 |
| 32 | 35.94 | 35.62 | 34.86 | 36.64 | 47.96 |
| 33 | 21.27 | 19.71 | 22.69 | 21.81 | 27.48 |
| 34 | 41.69 | 42.08 | 41.88 | 40.90 | 49.55 |
| 35 | 51.20 | 49.32 | 52.00 | 51.89 | 64.79 |
| 36 | 21.59 | 21.74 | 21.64 | 22.61 | 23.16 |
| 37 | 34.30 | 33.71 | 10.12 | 12.97 | 38.38 |
| 38 | 40.57 | 41.11 | 40.23 | 39.81 | 49.52 |
| 39 | 37.11 | 38.17 | 38.49 | 38.57 | 44.95 |
| 40 | 47.18 | 49.53 | 48.48 | 49.33 | 58.60 |
| 41 | 32.89 | 33.05 | 33.28 | 32.84 | 38.01 |
| 42 | 9.66 | 7.96 | 9.44 | 8.77 | 9.75 |
| 43 | 10.13 | 8.49 | 8.06 | 8.72 | 8.93 |
| 44 | 14.32 | 15.41 | 14.05 | 15.33 | 13.82 |
| 45 | 16.99 | 15.81 | 15.70 | 16.11 | 14.16 |
| 46 | 29.19 | 29.97 | 29.28 | 31.06 | 33.05 |
| 47 | 33.65 | 30.73 | 32.82 | 28.10 | 43.28 |
| 48 | 10.63 | 8.97 | 10.38 | 10.32 | 11.65 |
| 49 | 31.51 | 38.29 | 30.06 | 25.62 | 35.89 |
| 50 | 46.90 | 45.35 | 47.67 | 46.43 | 48.74 |
| 51 | 8.95 | 8.64 | 8.35 | 7.74 | 9.53 |
| 52 | 3.72 | 3.70 | 3.38 | 4.47 | 3.31 |
| 53 | 17.92 | 17.41 | 18.88 | 19.40 | 19.42 |
| 54 | 18.83 | 18.85 | 20.05 | 18.60 | 22.48 |
| 55 | 7.41 | 7.50 | 8.09 | 7.64 | 9.01 |
| 56 | 23.12 | 19.38 | 21.53 | 21.13 | 20.07 |
| 57 | 10.79 | 11.22 | 11.10 | 12.84 | 10.52 |
| 58 | 18.42 | 17.32 | 15.00 | 15.13 | 14.87 |
| 59 | 12.32 | 10.69 | 12.26 | 12.74 | 12.46 |
| 60 | 8.88 | 8.78 | 9.88 | 7.89 | 9.24 |
| 61 | 9.44 | 11.16 | 9.86 | 11.03 | 8.39 |
| 62 | 12.39 | 11.87 | 11.67 | 11.60 | 6.11 |
| 63 | 12.59 | 12.78 | 10.70 | 13.11 | 11.85 |
| 64 | 19.00 | 19.70 | 16.90 | 19.48 | 19.38 |
| 65 | 24.91 | 26.24 | 26.41 | 25.48 | 23.33 |

| | ms.conc.1 | ws.conc.1 | ms.conc.2 | ws.conc.2 | frm |
|----|-----------|-----------|-----------|-----------|-------|
| 66 | 12.42 | 15.42 | 13.05 | 13.68 | 15.70 |
| 67 | 7.43 | 6.66 | 7.79 | 5.42 | 8.01 |
| 68 | 20.96 | 20.80 | 20.74 | 21.40 | 19.32 |
| 69 | 4.26 | 3.31 | 4.87 | 4.71 | 4.46 |
| 70 | 11.84 | 11.67 | 12.72 | 13.36 | 12.60 |
| 71 | 7.70 | 10.00 | 9.03 | 10.15 | 8.84 |
| 72 | 23.25 | 24.47 | 22.56 | 23.97 | 23.98 |
| 73 | 17.63 | 16.57 | 16.39 | 16.64 | 16.74 |
| 74 | 11.89 | 11.58 | 8.65 | 8.50 | 9.26 |
| 75 | 15.16 | 14.97 | 15.93 | 12.48 | 13.37 |
| 76 | 13.46 | 15.45 | 15.42 | 15.53 | 12.76 |
| 77 | 19.51 | 20.12 | 19.12 | 20.49 | 17.46 |

PM_{2.5} Time Plot



PM_{2.5} Distributions Are Lognormal



Sample Computations

To compute and print the summary table for accuracy and precision using the original data values:

```
> library(merror)
> data(pm2.5)
> ncb.od(pm2.5)$sigma.table
```

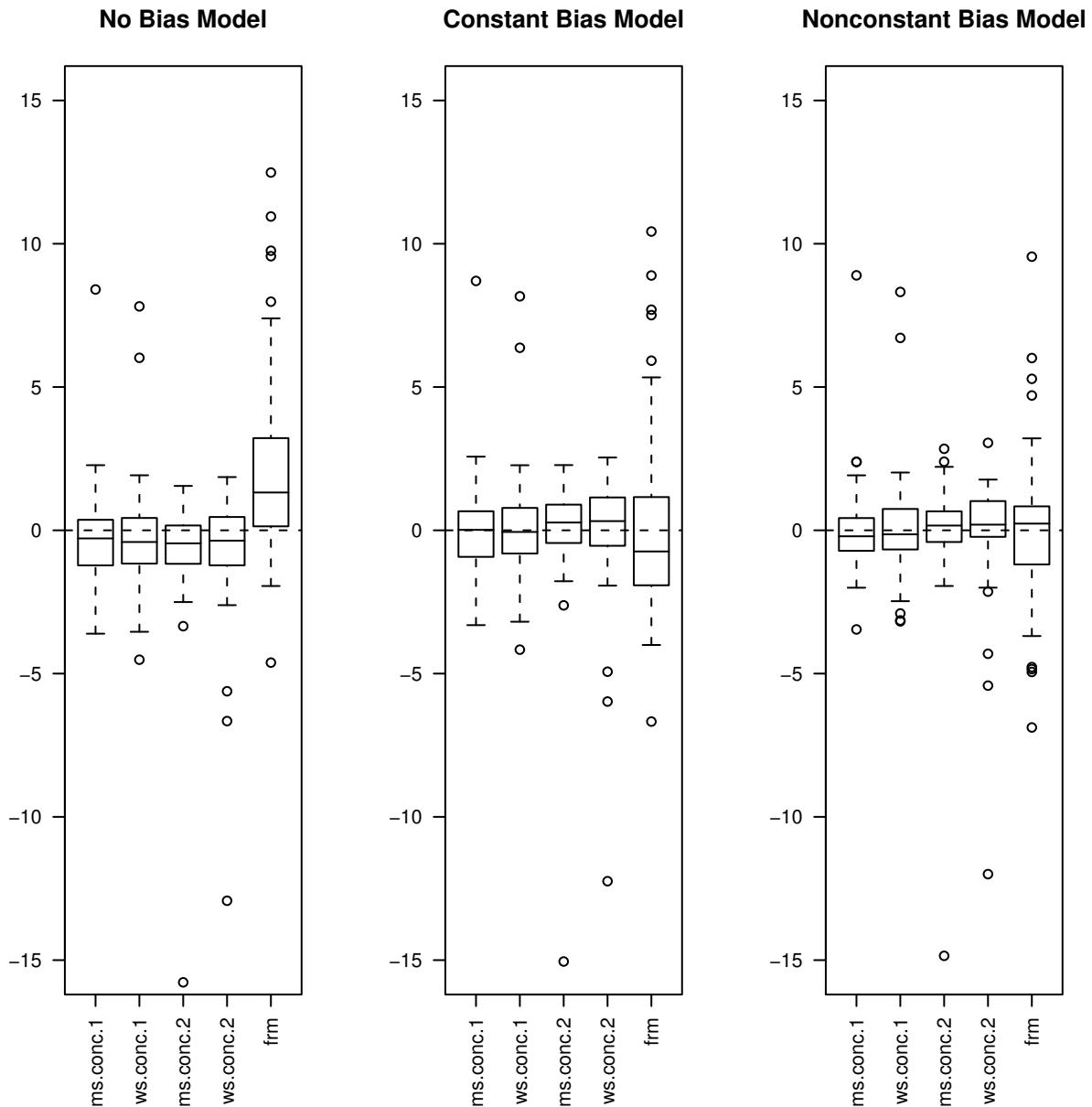
To compute and plot the errors under the nonconstant bias model for the federal reference method sampler:

```
> qqnorm(errors.ncb(pm2.5))
```

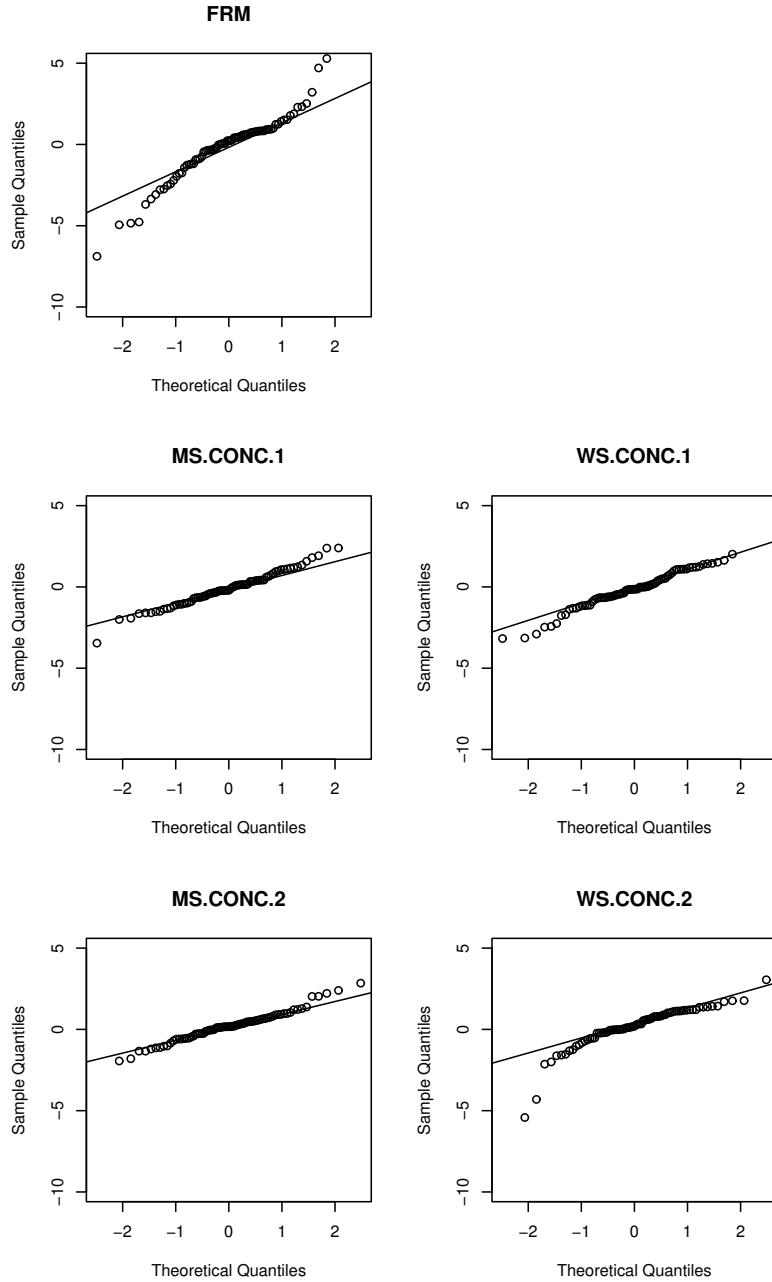
or

```
> qqnorm(ncb.od(pm2.5)$errors.ncb)
```

Measurement Error Box Plots



Measurement Error Normal Plots



Nonconstant Bias Model (OD) Summary

```
> ncb.od(pm2.5)$sigma.table
```

| i | n | $\hat{\sigma}_i$ | $\hat{\sigma}_{\hat{\sigma}_i}$ | $\bar{\alpha}_i$ | $\bar{\beta}_i$ | ν | $\chi^2_{q,\nu}$ | | 95% C. I. | |
|-----------|-----|------------------|---------------------------------|------------------|-----------------|-------|------------------|-------------|-----------|-------|
| | | | | | | | $q = 0.025$ | $q = 0.975$ | Lower | Upper |
| ms.conc.1 | 77 | 1.14 | 0.63 | 0.50 | 0.96 | 21.92 | 10.93 | 36.68 | 0.88 | 1.62 |
| ws.conc.1 | 77 | 1.42 | 0.68 | 0.27 | 0.97 | 37.50 | 22.49 | 56.28 | 1.16 | 1.83 |
| ms.conc.2 | 77 | 2.57 | 1.11 | 0.08 | 0.96 | 57.14 | 38.14 | 79.92 | 2.17 | 3.14 |
| ws.conc.2 | 77 | 2.52 | 1.09 | 0.32 | 0.95 | 55.97 | 37.18 | 78.53 | 2.13 | 3.09 |
| frm | 77 | 2.72 | 1.16 | -1.52 | 1.17 | 60.22 | 40.66 | 83.55 | 2.31 | 3.31 |
| Process | 77 | 11.71 | 4.71 | | | 76.31 | 54.05 | 102.36 | 10.11 | 13.92 |

Constant Bias Model (OD) Summary

```
> ncb.od(pm2.5, beta=rep(1, 5))$sigma.table
```

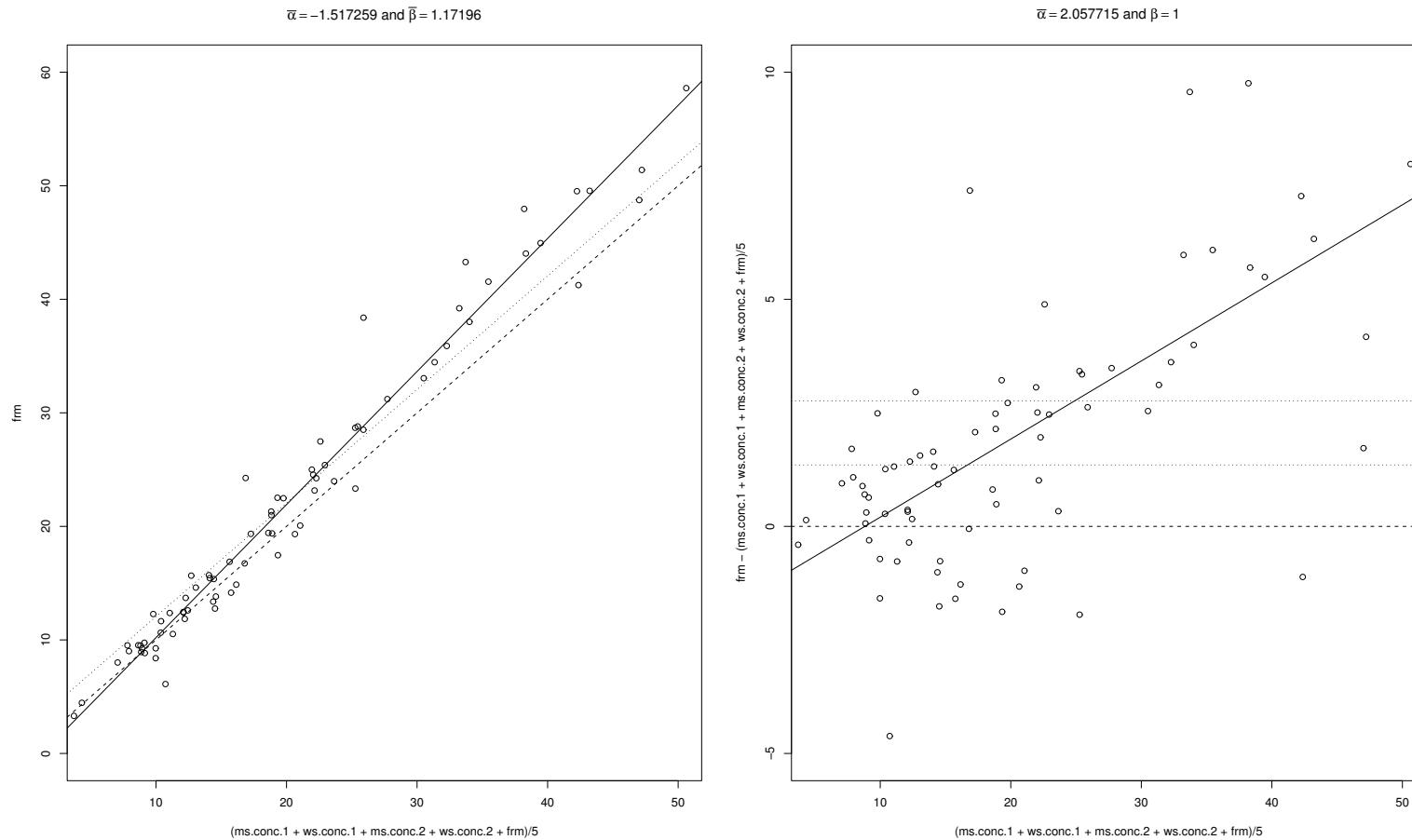
| i | n | $\widehat{\sigma}_i$ | $\widehat{\sigma}_{\widehat{\sigma}_i}$ | $\bar{\alpha}_i$ | β_i | ν | $\chi^2_{q,\nu}$ | | 95% C. I. | |
|-----------|-----|----------------------|---|------------------|-----------|-------|------------------|-------------|-----------|-------|
| | | | | | | | $q = 0.025$ | $q = 0.975$ | Lower | Upper |
| ms.conc.1 | 77 | 1.15 | 0.65 | -0.30 | 1.00 | 19.08 | 8.96 | 32.95 | 0.87 | 1.67 |
| ws.conc.1 | 77 | 1.40 | 0.69 | -0.35 | 1.00 | 34.41 | 20.12 | 52.47 | 1.13 | 1.83 |
| ms.conc.2 | 77 | 2.57 | 1.13 | -0.73 | 1.00 | 53.87 | 35.48 | 76.04 | 2.16 | 3.16 |
| ws.conc.2 | 77 | 2.54 | 1.12 | -0.68 | 1.00 | 52.62 | 34.47 | 74.55 | 2.13 | 3.13 |
| frm | 77 | 3.70 | 1.52 | 2.06 | 1.00 | 70.30 | 49.01 | 95.38 | 3.18 | 4.43 |
| Process | 77 | 11.39 | 4.58 | | | 76.24 | 53.99 | 102.28 | 9.83 | 13.53 |

Constant Bias Model (PD) Summary

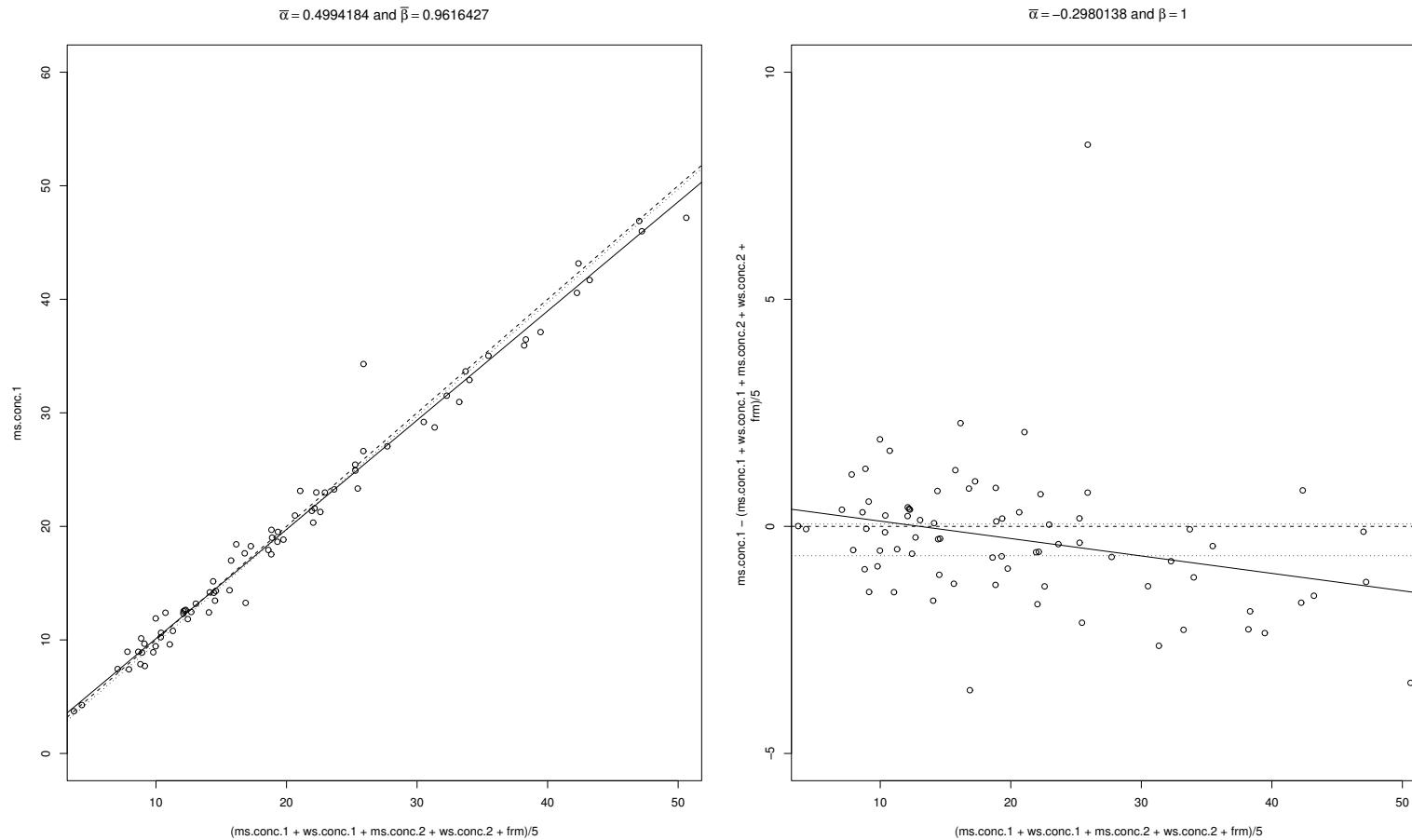
```
> cb.pd(pm2.5)$sigma.table
```

| i | n | $\hat{\sigma}_i$ | $\hat{\sigma}_{\hat{\sigma}_i}$ | $\bar{\alpha}_i$ | β_i | ν | $\chi^2_{q,\nu}$ | | 95% C. I. | |
|-----------|-----|------------------|---------------------------------|------------------|-----------|-------|------------------|-------------|-----------|-------|
| | | | | | | | $q = 0.025$ | $q = 0.975$ | Lower | Upper |
| ms.conc.1 | 77 | 1.16 | 0.66 | -0.30 | 1.00 | 19.72 | 9.40 | 33.80 | 0.89 | 1.68 |
| ws.conc.1 | 77 | 1.40 | 0.69 | -0.35 | 1.00 | 33.68 | 19.56 | 51.56 | 1.13 | 1.83 |
| ms.conc.2 | 77 | 2.57 | 1.13 | -0.73 | 1.00 | 53.93 | 35.53 | 76.11 | 2.16 | 3.17 |
| ws.conc.2 | 77 | 2.54 | 1.12 | -0.68 | 1.00 | 52.91 | 34.71 | 74.90 | 2.14 | 3.14 |
| frm | 77 | 3.66 | 1.51 | 2.06 | 1.00 | 70.08 | 48.82 | 95.12 | 3.14 | 4.39 |

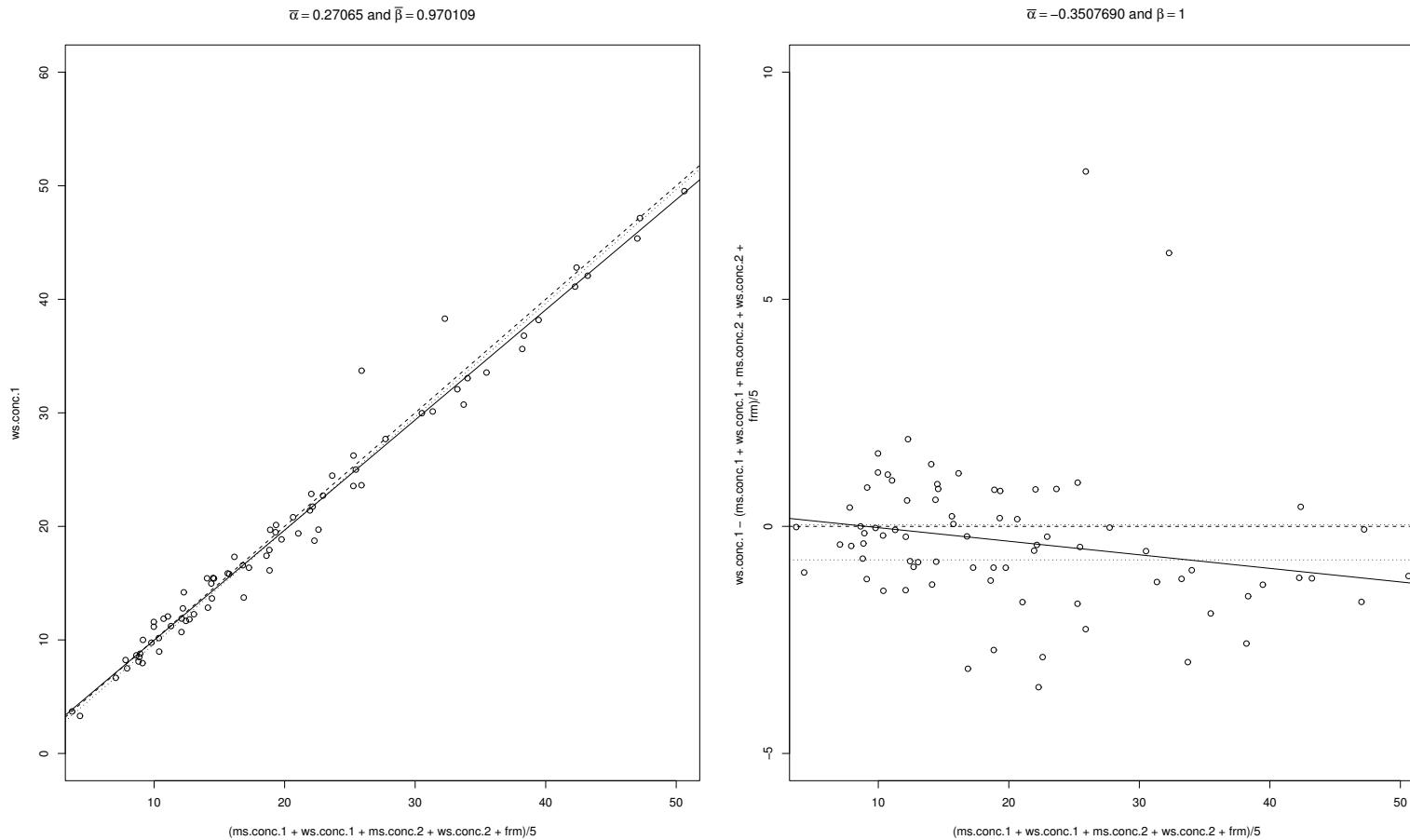
FRM Accuracy



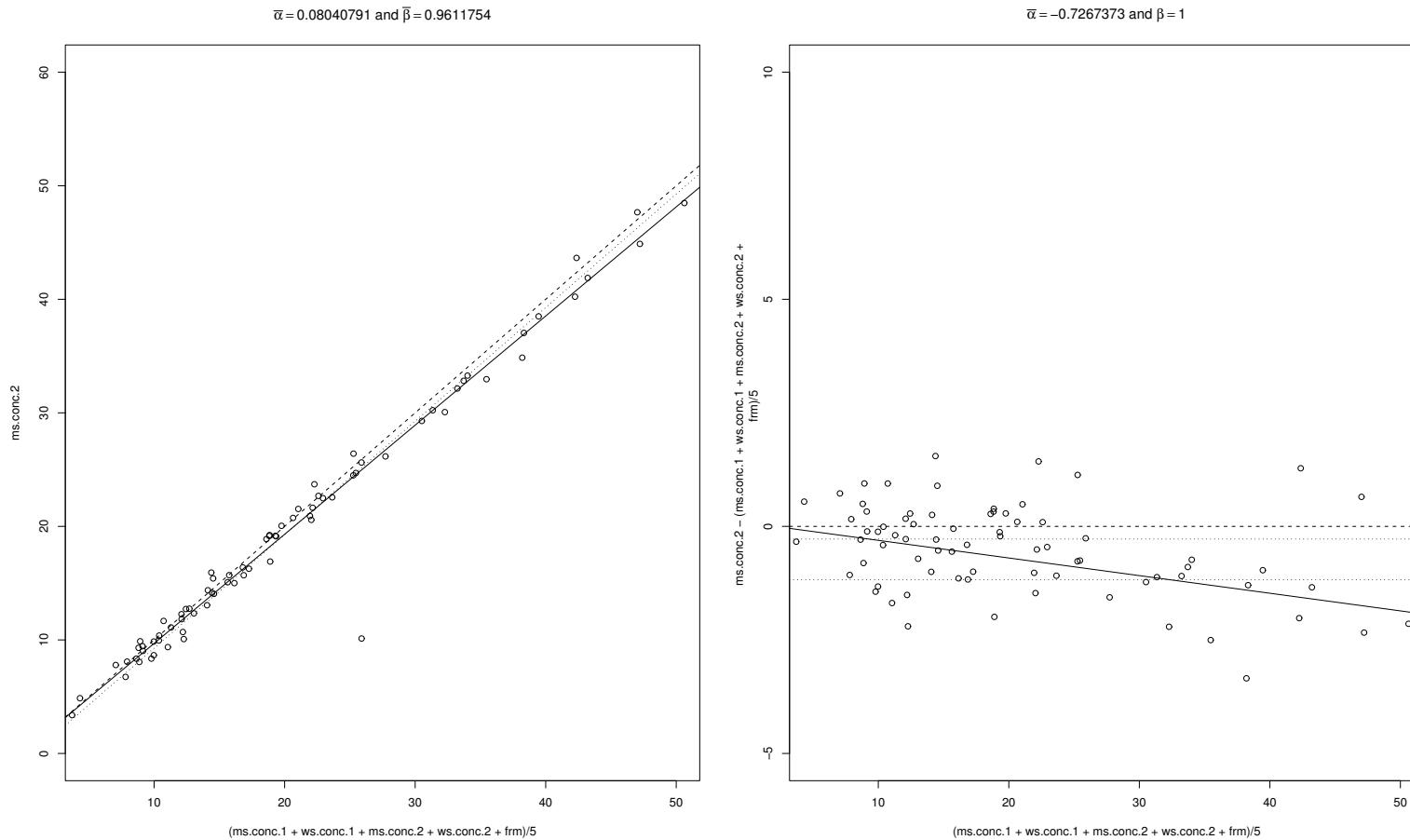
Personal Sample 1 - MS



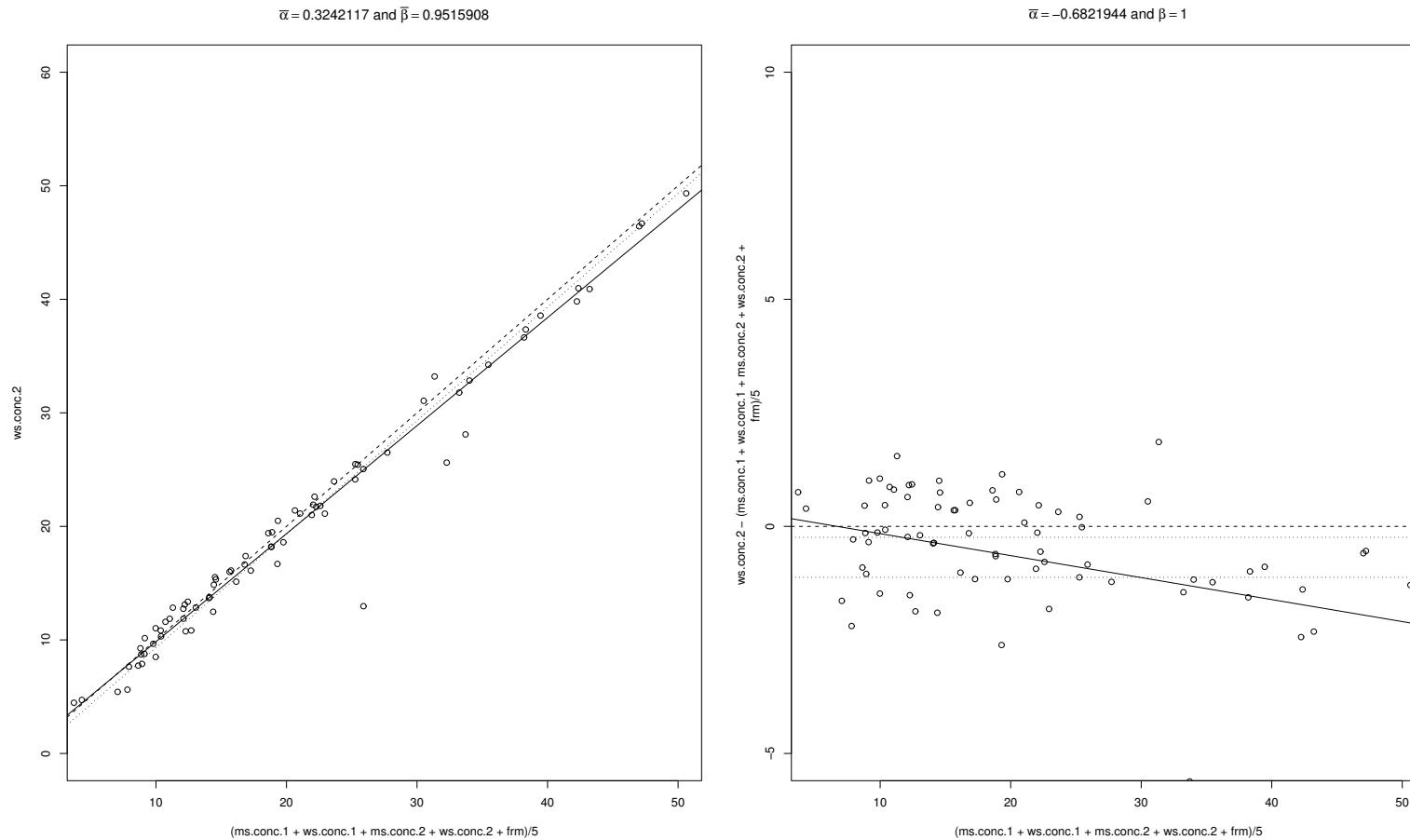
Personal Sampler 1 - WS



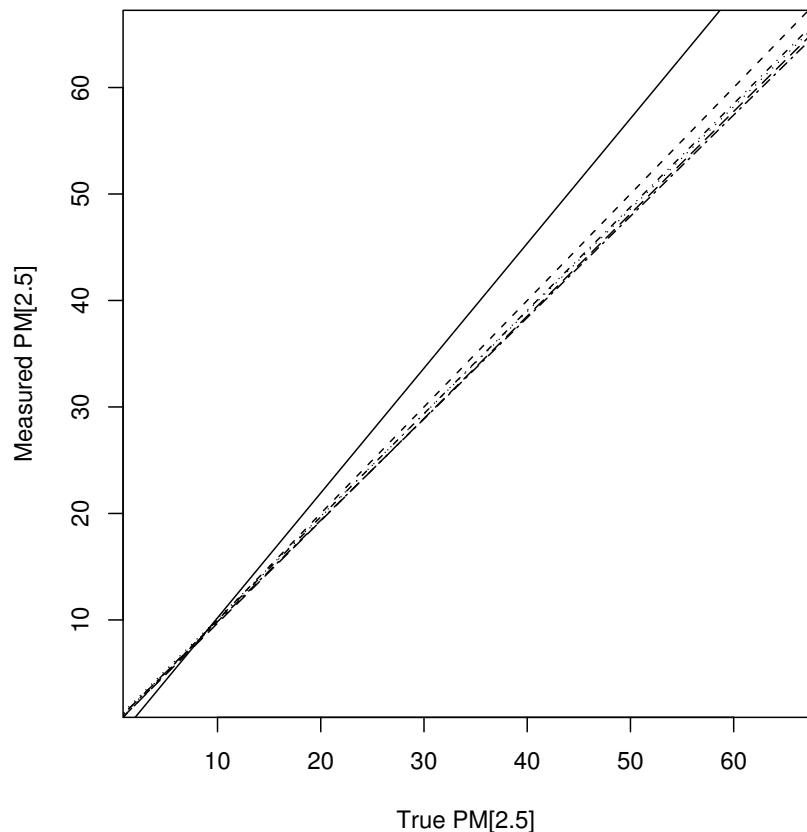
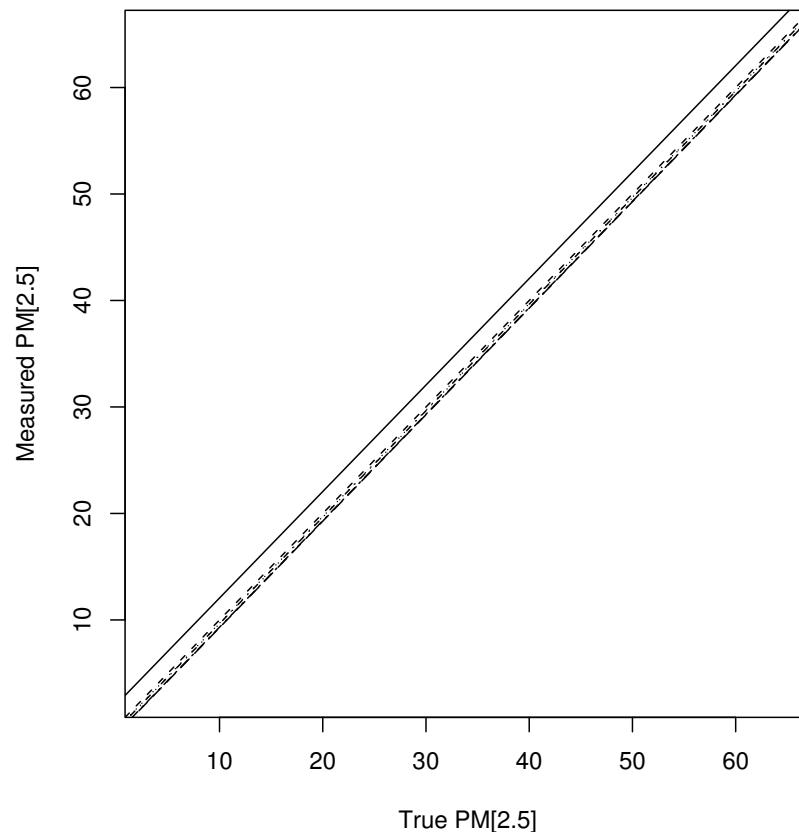
Personal Sampler 2 - MS



Personal Sampler 2 - WS



Relative Accuracy

Nonconstant Bias Model**Constant Bias Model**

Likelihood Ratio Test - All Filters

```
> lrt(pm2.5)

$N.methods
[1] 5

$n.items
[1] 77

$beta.bars
ms.conc.1 ws.conc.1 ms.conc.2 ws.conc.2      frm
0.9616427 0.9701091 0.9611754 0.9515908 1.1719601

$\lambda
[1] 42.8864

$df
[1] 4

$p.value
[1] 1.092498e-08
```

Likelihood Ratio Test - Personal Filters

```
> lrt(pm2.5[,1:4])
$N.methods
[1] 4

$n.items
[1] 77
$beta.bars
ms.conc.1 ws.conc.1 ms.conc.2 ws.conc.2
0.9968092 1.0058383 1.0038545 0.9935484

$\lambda
[1] 0.2335192

$df
[1] 3

$p.value
[1] 0.972005
```

Bias Estimates for Constant Bias Model ANOVA

| | Df | Sum Sq | Mean Sq | F value | Pr(>F) |
|-------------|-----|----------|---------|---------|---------|
| air parcels | 76 | 53304.03 | 701.37 | 120.43 | <0.0001 |
| samplers | 4 | 418.85 | 104.71 | 17.98 | <0.0001 |
| Residuals | 304 | 1770.49 | 5.82 | | |

Bias Estimates for Constant Bias Model

| Sampler/Filter | Bias α | 95% S. C. I. | |
|----------------|------------------|--------------|-------|
| | | Lower | Upper |
| FRM | 2.06 | 1.43 | 2.69 |
| MS.CONC.1 | -0.30 | -0.93 | 0.33 |
| WS.CONC.1 | -0.35 | -0.98 | 0.28 |
| MS.CONC.2 | -0.73 | -1.36 | -0.09 |
| WS.CONC.2 | -0.68 | -1.31 | -0.05 |

Personal Sampler Estimates - Separate Filters

| Sampler | $\hat{\sigma}_i$ | $\hat{\sigma}_{\hat{\sigma}_i}$ | 95% C. I. | |
|---------|------------------|---------------------------------|-----------|-------|
| | | | lower | upper |
| conc.1 | 0.91 | 0.46 | 0.72 | 1.24 |
| conc.2 | 1.80 | 0.78 | 1.52 | 2.23 |

Personal Sampler Estimates - Averaging Filters First

| i | n | $\widehat{\sigma}_i$ | $\widehat{\sigma}_{\widehat{\sigma}_i}$ | $\bar{\alpha}_i$ | $\bar{\beta}_i$ | ν | $\chi^2_{q,\nu}$ | | 95% C. I. | |
|---------|-----|----------------------|---|------------------|-----------------|--------|------------------|-------------|-----------|-------|
| | | | | | | | $q = 0.025$ | $q = 0.975$ | Lower | Upper |
| frm | 77 | 2.58 | 1.25 | -1.42 | 1.15 | 36.154 | 21.454 | 54.626 | 2.10 | 3.35 |
| conc.1 | 77 | 1.19 | 0.90 | 0.50 | 0.94 | 6.326 | 1.380 | 14.965 | 0.78 | 2.56 |
| conc.2 | 77 | 2.59 | 1.15 | 0.60 | 0.92 | 52.409 | 34.299 | 74.298 | 2.18 | 3.21 |
| Process | 77 | 11.98 | 4.83 | | | 75.864 | 53.668 | 101.842 | 10.34 | 14.25 |

Calibration

$$PS = 0.55 + 0.93 \times (\text{True Concentration})$$

$$FRM = -1.42 + 1.15 \times (\text{True Concentration})$$

So

$$PS = 1.70 + 0.81 \times FRM$$

and

$$PS - FRM = 1.97 - 0.22 \times (\text{True Concentration})$$

This implies at a true concentration of $50 \mu\text{g m}^{-3}$ a bias of about $9 \mu\text{g m}^{-3}$ and a zero bias when the true concentration is about $9 \mu\text{g m}^{-3}$. When the true concentration is below $9 \mu\text{g m}^{-3}$, the personal sampler concentration is higher than the FRM. This reverses above a true concentration of $9 \mu\text{g m}^{-3}$.

Conclusions

- Regression analysis CANNOT be used to assess accuracy and precision.
- Nonconstant bias model must be used.
- Measurement errors are approximately Normal.
- $\text{PM}_{2.5}$ samplers have excellent precision - on the order of $2\text{-}3 \mu\text{g m}^{-3}$.
- Bias between the FRM and the personal samplers is small but nonconstant.

Software Used

No commercial, proprietary software was used to do the computations or to make the foils:

- All software was run under the Gnu/Linux operating system.
- *tex* and *latex* were used for typesetting.
- *LyX* was used as a graphical user interface to *tex* and *latex* using the *FoilTex* document class.
- R was used for all computations and graphs. Besides the *merror* package, the *xtable* package was used to convert the tables to *tex*, and then *reLyX* was used to convert from *latex* to *LyX* format.
- Ghostscript was used for viewing and for printing.